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Fatigue-resistant high-performance elastocaloric materials made by additive manufacturing

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Abstract

Elastocaloric cooling, a solid-state cooling technology, exploits the latent heat released and absorbed by stress-induced phase transformations. Hysteresis associated with transformation, however, is detrimental to efficient energy conversion and functional durability. We have created thermodynamically efficient, low-hysteresis elastocaloric cooling materials by means of additive manufacturing of nickel-titanium. The use of a localized molten environment and near-eutectic mixing of elemental powders has led to the formation of nanocomposite microstructures composed of a nickel-rich intermetallic compound interspersed among a binary alloy matrix. The microstructure allowed extremely small hysteresis in quasi-linear stress-strain behaviors—enhancing the materials efficiency by a factor of four to seven—and repeatable elastocaloric performance over 1 million cycles. Implementing additive manufacturing to elastocaloric cooling materials enables distinct microstructure control of high-performance metallic refrigerants with long fatigue life.

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Fatigue-resistant high-performance elastocaloric materials via additive manufacturing

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Abstract:

Elastocaloric cooling, a solid-state cooling technology, exploits the latent heat released and absorbed by stress-induced phase transformations. Hysteresis associated with transformation, however, is detrimental to efficient energy conversion and functional durability. We have created thermodynamically efficient, low-hysteresis elastocaloric cooling materials via additive manufacturing of Nickel–Titanium. The use of localized molten environment and near-eutectic mixing of elemental powders has led to the formation of nanocomposite microstructures composed of a Nickel-rich intermetallic compound interspersed amongst binary alloy matrix. The microstructure allowed extremely small hysteresis in quasi-linear stress-strain behaviors—enhancing the materials efficiency by a factor of four to seven—and repeatable elastocaloric performance over one million cycles. Implementing additive manufacturing to elastocaloric cooling materials enables unique microstructure control of high-performance metallic refrigerants with long fatigue life.

One Sentence Summary: 3D printing produces high-efficiency solid-state cooling

nanocomposite materials with long fatigue life.

Main Text:

Space cooling and refrigeration consume ~one-fifth of the entire electricity demand worldwide (1). Vapor compression, which dominates the market, is a mature technology, but its efficiency has plateaued, and the high global-warming potential of its refrigerants remains a major concern. Solid-state cooling technologies including thermoelectric (2) and passive radiative cooling (3) represent attractive green alternatives to vapor compression. Particularly promising are caloric (magnetocaloric, mechanocaloric, and electrocaloric) cooling techniques (4-7), which have the potential to surpass the efficiency of vapor compression. Because caloric materials enlist active heat-pumping through manipulation of their functional properties (i.e., magnetization, stress-state, and electric polarization) (7), they can be exploited for giant cooling effects. However, hysteresis in the properties is their Achilles heel since it represents work lost in every heat-pumping cycle as dissipated heat, and it can ultimately lead to materials fatigue and failure. The long-term fatigue properties are critical for applications of caloric materials, yet their evaluation over a large number of cycles is not common.

The martensitic phase transformation of shape memory alloys (SMAs) may manifest in dramatic temperature-triggered shape change, enabling solid-state actuation technologies (8). The martensitic transformation can also be triggered by stress, resulting in superelasticity (9). During superelastic cycles, latent heat is released/absorbed upon loading/unloading due to the exothermic/endothermic nature of the phase transformation. This stress-induced heat-pumping of SMAs is elastocaloric cooling (10, 11), one type of mechanocaloric cooling. Adiabatic temperature change (ΔT_{ad}) of elastocaloric materials can be as large as 31.5 K (12), and the largest reported isothermal entropy change (ΔS) of an SMA is 70.7 J kg⁻¹ K⁻¹ (13). Such unparalleled cooling potential has made elastocaloric cooling a front runner among the crowded field of alternative cooling technologies (14). Functioning elastocaloric cooling prototypes with

capacity over 100 W has been developed (15), while elastocaloric regenerative heat pumps with ΔT_{ad} as large as 19 K has been demonstrated using commercially available Nickel–Titanium (Ni–Ti) materials (16, 17). However, thermomechanical hysteresis of elastocaloric SMAs can limit the efficiency of cooling devices, and its impact on long-term performance has not been addressed.

We synthesized elastocaloric materials consisting of alloy matrix and intermetallic phases arranged in nanocomposite microstructures using the powder-feed laser directed-energy-deposition (L-DED) technique. This method results in a local melting of metal powders followed by rapid solidification (18, 19). When a Ni-rich blend of elemental Ni and Ti powders are mixed during this process, nanocomposite microstructures—comprised of transforming, elastocaloric binary NiTi alloy matrix and a non-transforming Ni_3Ti intermetallic phase—form in a two-phase mixture of comparable volume fractions, with intricate dendritic structures. This unique configuration enlists the non-transforming intermetallic phase for biasing the phase transformation leading to considerable improvement in elastocaloric efficiency and transformation reversibility through work hysteresis minimization.

The L-DED produced Ni–Ti nanocomposite exhibits substantially reduced hysteresis with a quasi-linear stress-strain behavior resulting in a multi-fold increase in the materials efficiency, defined as the ratio of materials coefficient of performance ($COP_{materials}$) to Carnot COP . We show that the elastocaloric thermodynamic cycle of these materials is stable over more than a million cycles. In contrast to rate-dependent hysteresis commonly observed in traditionally processed SMAs (20, 21), the hysteresis of the L-DED Ni–Ti nanocomposite is nearly rate-independent (from 0.0002 s^{-1} to 0.2 s^{-1}), facilitating high-frequency elastocaloric operations. We use a constitutive model and in situ synchrotron X-ray diffraction experiments to

confirm that their properties originate from kinematics of load transfer between transforming and non-transforming phases.

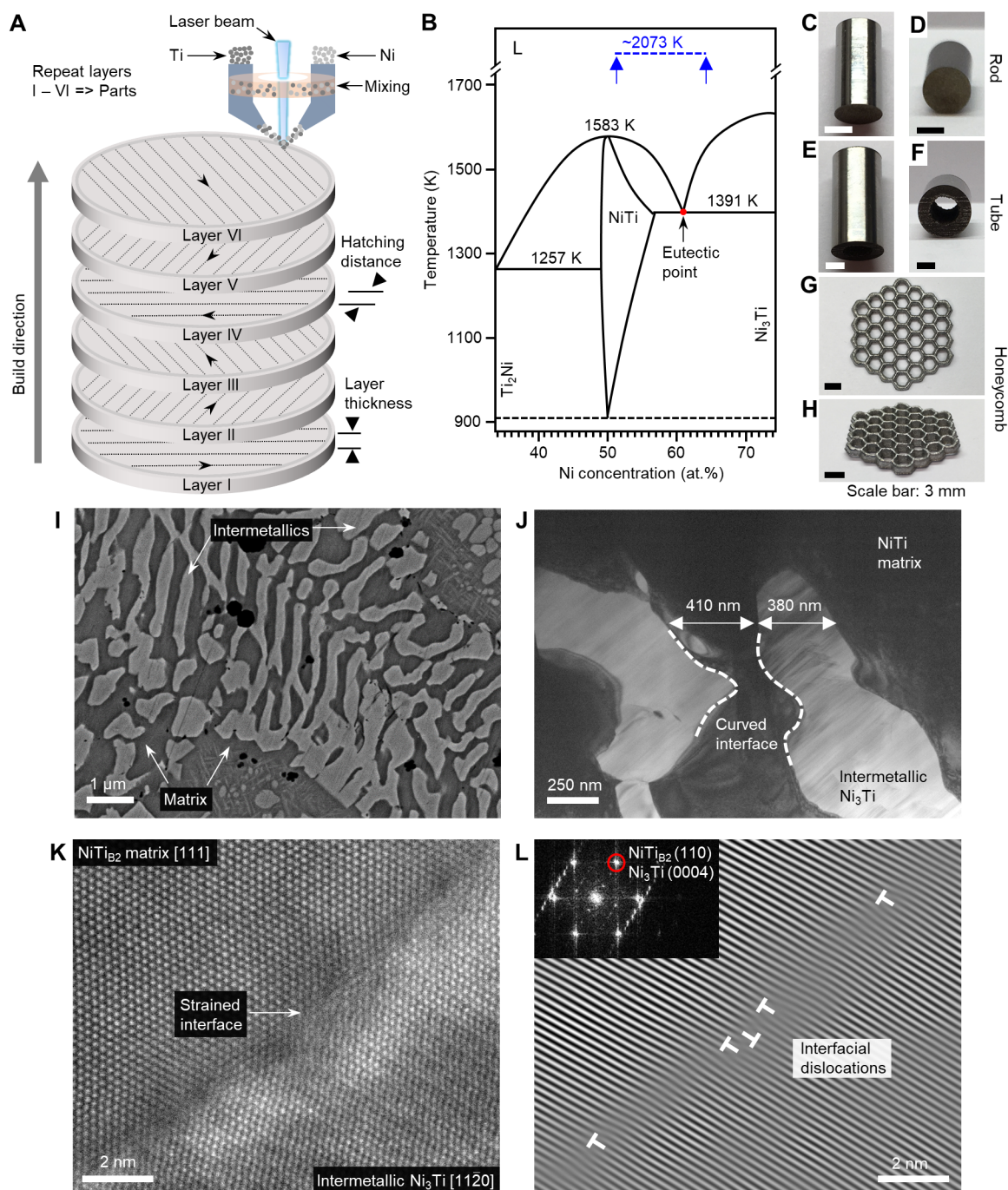


Fig. 1. Design of elastocaloric Ni-Ti nanocomposite by directed energy deposition. (A) Schematic representation of an L-DED process. Flows of Ni and Ti powders are individually controlled. The Ni and Ti powders are mixed and then fed to the laser beam. An induced molten pool moves to build materials layer by layer (Fig. S1). (B) Phase diagram of Ni-Ti (adapted with permission from (22)) highlighting in blue the Ni-rich composition near a eutectic point and the molten pool temperature used in this work. (C)-(H) Photographs of L-DED produced Ni-Ti nanocomposite rods, tubes, and honeycombs in top (C),(E),(G) and front (D),(F),(H) views, respectively. (I)-(K) SEM image (I), bright-field TEM image (J), and high-resolution HAADF-

STEM image (K) of as-built $\text{Ni}_{51.5}\text{Ti}_{48.5}/\text{Ni}_3\text{Ti}$ nanocomposite. In (I), the regions with different contrasts are crystallographically identified to be NiTi and Ni_3Ti phases (Figs. S2 and S3). In (J), typical curved interfaces are delineated. In (K) (a zoomed-in view of a curved interface), NiTi and Ni_3Ti phases have an orientation relationship of $\text{NiTi}_{[111]} \parallel \text{Ni}_3\text{Ti}_{[11\bar{2}0]}$, although each is slightly off the zone axis due to lattice strains within the interface (Fig. S4). (L) Inverse fast Fourier transform (IFFT) image from the circled spot in the FFT image (inset; generated from (K)). Interfacial dislocations are identified and marked with T symbols.

The key features of the L-DED process (Fig. 1A) are a millimeter-scale molten pool of mixed powders and a rapid cooling rate of more than 10^3 K s^{-1} (23). Metal nanocomposites made by, for example, melt-casting (24), can display a stress-transfer mechanism responsible for high strength, a desirable attribute of functional alloys. Because eutectic solidification can naturally lead to the formation of composites, we used the eutectic point in the Ni-rich composition range (Fig. 1B) of binary Ni–Ti to obtain elastocaloric nanocomposite using L-DED (25). Optimization of processing parameters (such as layer thickness, hatching space) was guided by a normalized processing map (26) for high denseness ($\approx 99\%$) and mechanical integrity, and the molten pool temperature in operation was maintained to be 1,973–2,173 K, as measured in situ by a ThermoViz pyrometer. We adjusted the ratio of the flow rate of elemental Ni and Ti powders to print different compositions of Ni–Ti materials in a range of geometries (Fig. 1, C to H).

Rapid cooling of the molten pool during L-DED enables precipitation from off-eutectic compositions in a volume fraction comparable to that of eutectic structures, as predicted by Scheil model (23, 27). We observed a substantial fraction of precipitates (up to $\approx 50\%$) in a wide compositional range of the Ni–Ti produced by L-DED (Fig. 1B). Curved microstructures can nucleate and grow, because the temperature gradient (highest at center and lowest at periphery) of the molten pool leads to circulation of mass and heat within the pool driven by Marangoni shear stress (28), thereby creating local perturbations of solute concentration and equilibrium temperature (29) on solid–liquid interfaces and breaking up the plane front in growth of steady-state eutectics. As a result of non-equilibrium conditions, a typical microstructure of L-DED produced Ni–Ti nanocomposite consists of transforming NiTi and non-transforming Ni_3Ti phases with large aspect ratios, curved interfaces, and comparable volume fractions (Fig. 1I). The size scale of the microstructure is inversely proportional to the cooling rate (27), which is at least two

orders of magnitude higher in L-DED than that of casting ($\approx 0.1 \text{ K s}^{-1}$) leading to a mixture of two phases at a submicrometer scale (Fig. 1J).

Large interfacial curvatures between the cubic B2-ordered NiTi phase and the hexagonal DO_{24} -ordered Ni_3Ti phase (Fig. 1J) can be naturally accommodated with small lattice mismatches to make their interfaces semi-coherent. An atomic-scale view of the adjacent regions displays strained boundaries (Fig. 1K) where interfacial dislocations are located (Fig. 1L). Pre-existing sites of high nucleation potency such as dislocations have been reported to trigger atomic shearing for nucleation of martensite (30) where a nucleation energy barrier is lowered (or completely suppressed in the case of spontaneous growth (31)). These interfacial dislocations inherent to the curvatures and additional dislocations induced by mechanical pre-treatment (Fig. S5) therefore serve as pre-existing nucleation sites to reduce energy barriers for martensite during the forward transformation and for austenite during the reverse transformation. In addition, these same nucleation sites can act as “micro-pockets” to accommodate remnant austenite and martensite after forward and reverse transformations, respectively, thereby eliminating the necessity of barrier-overcoming stage for nucleation during cyclic loading. After proper self-organization, pre-straining, and pre-stressing (shakedown state, Fig. S5), the intricate nanoscale network of connected microstructure suppresses the dislocation motion (32) and limits transformation dissipation resulting in enhanced cyclic stability.

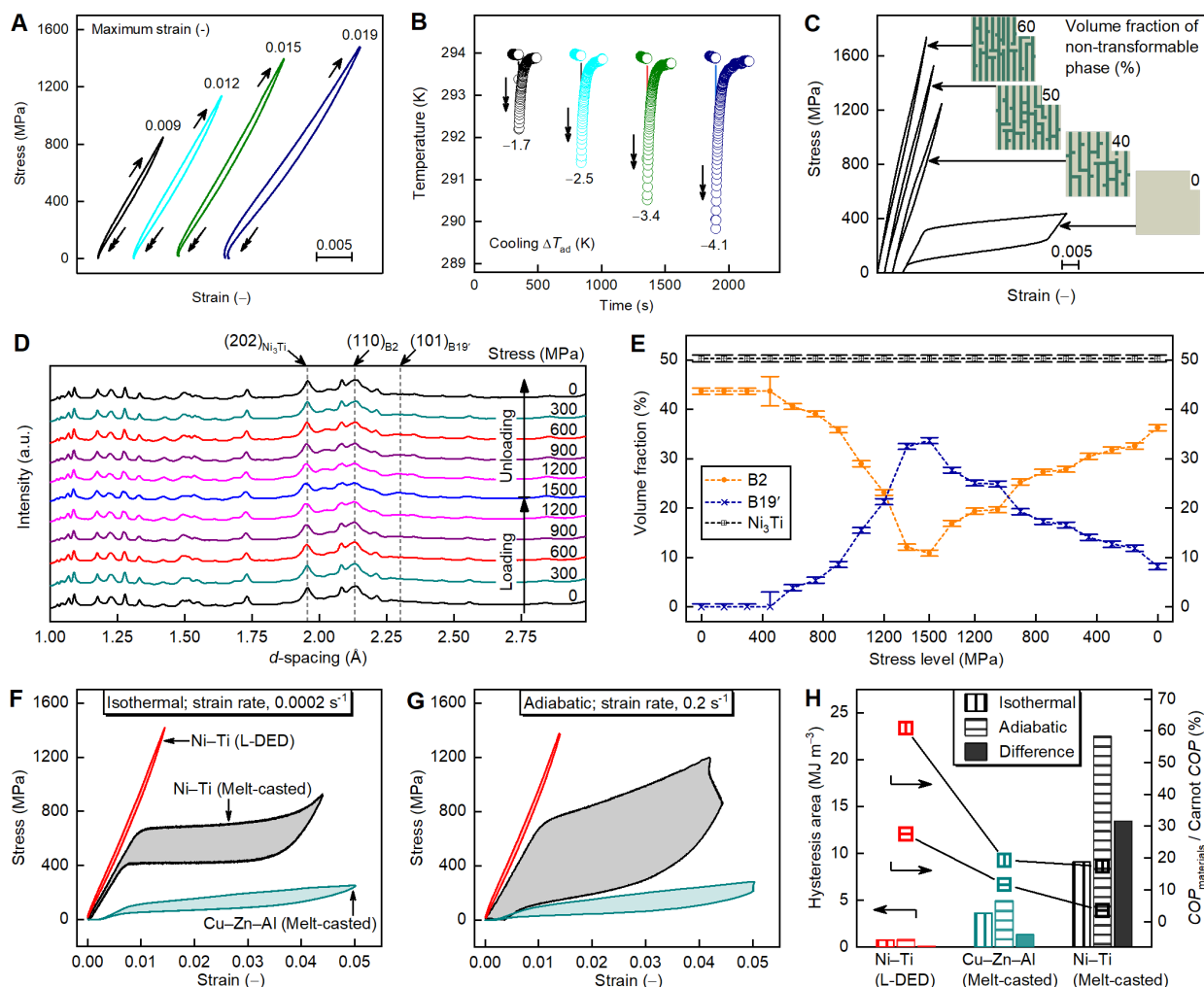


Fig. 2. Recoverable behaviors and elastocaloric properties of Ni-Ti nanocomposite. (A and B) The stress-strain curves (A) and corresponding elastocaloric cooling at room temperature (B) of L-DED produced Ni_{51.5}Ti_{48.5}/Ni₃Ti nanocomposite aged at 923 K for 3 hours. The single arrows in (A) denote loading, and the double arrows in (A) and (B) correspond to unloading. (C) Simulated stress-strain curves from a micromechanics model that accounts for the volume fraction of non-transforming phase (insets). (D and E) Synchrotron X-ray diffraction patterns during in situ loading-unloading (D) and the determined volume fraction of primary phases at different stress levels during the cycle (E). (F and G) Comparison of stress-strain curves for L-DED produced Ni_{51.5}Ti_{48.5}/Ni₃Ti nanocomposite and melt-casted Ni_{50.8}Ti_{49.2} and Cu₆₈Zn₁₆Al₁₆ alloys at the strain rate of 0.0002 s⁻¹ for isothermal loading/unloading (F) and 0.2 s⁻¹ for adiabatic loading/unloading (G). In (F) and (G), the area enclosed by the loading/unloading curves represents total dissipation energy per unit volume associated with hysteresis. (H) Comparison of hysteresis area under isothermal and adiabatic loading/unloading as well as the ratio of $COP_{materials}$ to Carnot COP for L-DED nanocomposite and melt-casted alloys at maximum transformations. The color code for each material is common for (F)–(H).

The L-DED produced Ni–Ti nanocomposite exhibits quasi-linear behaviors and substantially reduced hysteresis (Fig. 2A). The full strain recovery upon unloading is accompanied by a cooling ΔT_{ad} (Fig. 2B), a signature of martensitic transformation, which reaches 4.1 K. In a caloric cooling system, ΔT_{ad} of caloric materials can be boosted into a large temperature span across a device by active regeneration schemes (16, 33, 34). The quasi-linear recovery behavior arises from the load transfer between the non-transforming intermetallic phase and the transforming non-load-bearing phase, and has previously been also observed in melt-casted alloys after aging and/or cold-working (24, 35, 36). The effective modulus of the L-DED Ni–Ti nanocomposite (~80–90 GPa) is higher than the typical austenite (~50–60 GPa), which indicates the effect of the non-transforming intermetallic Ni_3Ti phase in the nanocomposite. As a result, as the austenite transforms to martensite, the intermetallic phase continues to carry the load elastically, and the resulting overall behavior is quasi-linear. To confirm this mechanism, we simulated the crossover from a regular superelastic to quasi-linear behavior by varying the volume fraction of non-transforming intermetallic phase and observed the appearance of quasi-linear behavior at a level of 40%, 50%, and 60% (Fig. 2C).

The small hysteresis we observed is due to the topology- and defect-controlled kinematics of numerous nucleation events and coalescence, where spatially dispersed pre-existing nucleation sites (Fig. 1L) favor continual, heterogeneous nucleation of new martensite followed by their coalescence. The resulting volumetric densities of obstacles that austenite-martensite transformation fronts meet in the course of transformation are reduced and require a decreased amount of frictional work to overcome, as observed in Cu–Zn–Al alloys (37). Additionally, the intermetallic phase has a large volume fraction ($\approx 50\%$), and it effectively guides the transformation process through elastic interaction with the transforming phase. This

process, in turn, tempers multiple instabilities occurring during traditional nucleation and fast growth and reduces energy dissipation and effective interfacial friction. We captured the progression in in situ synchrotron X-ray diffraction measurements (Fig. 2, D and E).

We attributed the commonly-observed rate-dependent hysteresis (e.g., the difference in hysteresis curves between Fig. 2F and 2G) to transformation-related heat in SMAs where surface convection dominates heat transfer. From an explicit integral equation of the specific dissipated energy ΔE (which is equal to the generated heat) (38), we can approximate ΔE as:

$$\Delta E \cong E_{\text{fr}} + \Delta T_{\text{ad}} \cdot \Delta s \quad (\text{eq. 1})$$

where E_{fr} is the irreversible specific energy that is the generated heat through interface friction,

ΔT_{ad} is the adiabatic change in temperature, and Δs is the specific entropy change associated with the phase transformation. The ΔE during a stress-strain cycle manifests itself as the hysteresis area (divided by density), and it increases with enlarged hysteresis. This relation can also explain the nearly rate-independent hysteresis we observed in Ni–Ti nanocomposite (Fig. 2H) where thermal conduction (thermal conductivity $\approx 18 \text{ W m}^{-1} \text{ K}^{-1}$) through a large volume fraction of non-transforming phase and surface convection (with convective heat transfer coefficient $\approx 4 \text{ W m}^{-2} \text{ K}^{-1}$) collectively facilitate effective heat transfer and rejection in a transformation cycle. In this instance, the second term on the right of Eq. 1 becomes small due to the rate of heat dissipation approaching the rate of heat generation.

Decreasing E_{fr} contributes to additional reduction in ΔE . In fact, E_{fr} consists of two components: $E_{\text{fr}} = E_{\text{f}} + E_{\text{p}}$ (39), where E_{f} is the heat dissipated from frictional work in a transformation cycle and E_{p} is the heat dissipated by plastic work within austenite-martensite interfaces due to their coherency loss. Although friction is ubiquitous in the propagation of austenite-martensite interfaces (40), reducing extended interfacial motions by having uniformly

distributed sites for nucleation and coalescence can substantially curtail frictions, leading to reduced E_f . The resultant minimization of E_f accounts for the substantial reduction in E_{fr} (Fig. 2H). In other alloy systems, relaxing local strain energy associated with phase transformation via improving lattice compatibility was found to lead to significant reduction in E_p (41-43). E_{fr} remains constant at different rates and plays a role in the rate-independence of hysteresis in the Ni-Ti nanocomposite.

Thermodynamics of cooling devices dictates that small hysteresis during isothermal loading/unloading in Stirling-like cycles leads to high efficiencies (15, 44). However, under the same heat exchange conditions as the Brayton-like cycle, Stirling-like operation cycles require much longer time per cycle (leading to reduced output wattage) and additional system components for effective heat transfer (44). In comparison, adiabatic loading/unloading in Brayton-like cycles (45) can operate much faster with relatively simple heat-exchange systems, albeit suffering from lower intrinsic efficiency due to the larger hysteresis (Fig. 2G).

$COP_{materials}$ in Brayton-like cycles are governed by the directly measured ΔT_{ad} with the adiabatic hysteresis, and $COP_{materials}$ in Stirling-like cycles are regulated by the latent heat with the isothermal hysteresis, based on thermodynamically derived equations with full work recovery (25). The hysteresis of L-DED Ni-Ti nanocomposite is extremely small in both cycles and has a negligible difference (indicating rate-independence). With a Carnot $COP = 37.5$ for $T_h = 308$ K and $T_c = 300$ K, the ratio of $COP_{materials}$ to Carnot COP of L-DED Ni-Ti nanocomposite is ≈ 7 times that of melt-casted Ni-Ti for adiabatic Brayton-like cycles (and ≈ 4 times that for isothermal Stirling-like cycles) at maximum transformations (Fig. 2H).

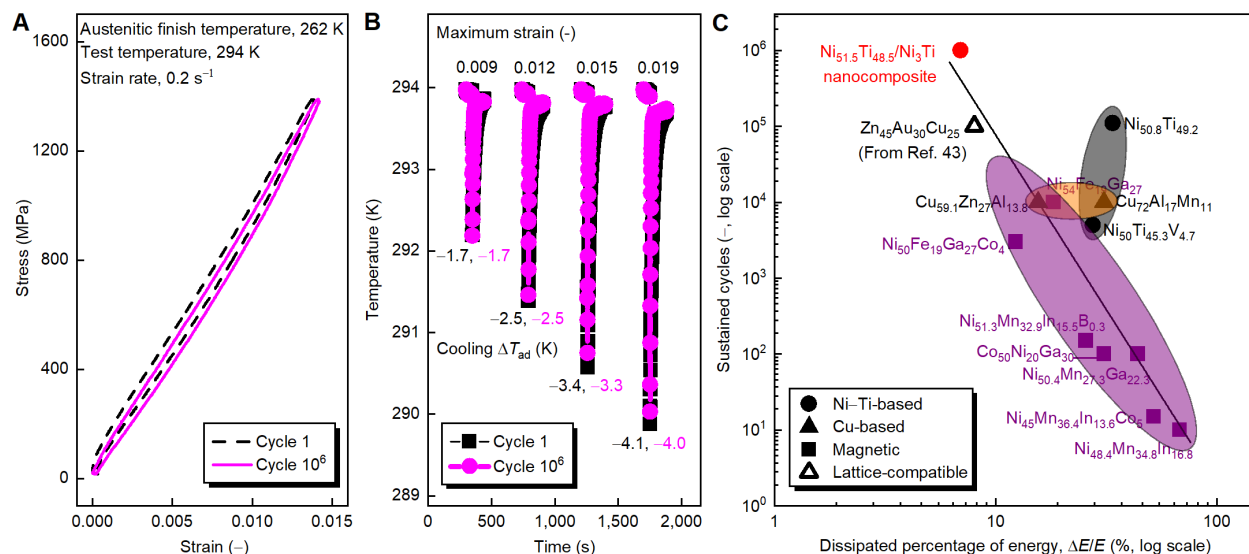


Fig. 3. Stability of Ni–Ti nanocomposite over one million compression cycles and comparison to other reported bulk elastocaloric materials. (A and B) Compressive stress-strain curves (A) and elastocaloric cooling (B) of L-DED produced $Ni_{51.5}Ti_{48.5}/Ni_3Ti$ nanocomposite aged at 923 K for 3 hours before and after one million cycles. (C) Log–log plot of the dissipated fraction of input energy, $\Delta E/E$, versus sustained compressive cycles for bulk elastocaloric materials in this work as well as those reported in the literature. A dissipated fraction of energy is the ratio of hysteresis area, ΔE , in a transformation cycle to the input energy, E . “Lattice-compatible” refers to the alloy where the lattice parameters of transformed and untransformed phases exhibit exceptional lattice compatibility (43). The straight line is a linear fit. The data from both polycrystalline and single-crystal materials are included. The numerical values used in this plot, as well as strain amplitude and references, are listed in Table S1.

We studied the long-term stability of the L-DED produced Ni–Ti nanocomposite. We found that the Ni–Ti nanocomposite is stable in their mechanical behavior and elastocaloric response for over 1 million cycles (Fig. 3, A and B), indicating their potential for use in regular commercial products with a typical ten-year life (operating at < 1 Hz (15)). This performance is in contrast to other cycled 3D-printed Ni–Ti materials (46, 47). Here, small hysteresis enabled by the nanostructured Ni₃Ti reinforcements is one important factor responsible for long-term stability. We previously showed that by tuning the lattice compatibility using stoichiometry in ternary alloys, we could minimize hysteresis of martensitic transformation and improve its reversibility to extended numbers of cycles (41, 48). However, a comparison of different SMA materials reveals that the absolute value of hysteresis is not the only determining factor. In fact, magnetic SMAs such as polycrystalline Ni–Mn–In and Ni–Fe–Ga (Table S1) seem to deteriorate quickly after a small number of cycles (~ 100) even with a hysteresis area as small as 1.2 MJ m^{-3} . For stress-induced fatigue, the endurance limit (that is, the stress amplitude able to attain a prescribed number of cycles, usually 10^7 , at zero mean stress) is proportional to the ultimate strength of materials by a factor of ≈ 0.33 (49). Across a spectrum of elastocaloric materials, it is the ratio of hysteresis area, ΔE , to the input work, E , that ultimately determines the number of cycles that the materials can sustain their performance over (Fig. 3C).

To understand this trend, we considered an analogy to the well-known S – N concept conceived by Wöhler in 1858 (50) that connects the stress amplitude (S) to the cycles to failure (N) in structural fatigue of materials and obtain a correlation of $\Delta E/E$ (hysteresis as a fraction of input energy) to the cycles to “functional failure”, N , (which we define as the number of cycles at the onset of loss of their functionality, Fig. 3C). In an ideal case of $\Delta E/E = 0$ (i.e., transformation with no hysteresis), the number of cycles to functional failure would

asymptotically approach infinity (or extremely large numbers). SMAs typically exhibit hysteresis in superelastic cycles; the best $\Delta E/E$ hitherto reported for cycling are from $\text{Zn}_{45}\text{Au}_{30}\text{Cu}_{25}$ alloys optimized through tuning the lattice parameters (43) and $\text{Ni}_{51.5}\text{Ti}_{48.5}/\text{Ni}_3\text{Ti}$ nanocomposite with friction-limited kinematics in this work, both of which possess an $\Delta E/E$ less than 10%. Because of similarity in the hysteresis behavior associated with input work among different materials, the energy-based $(\Delta E/E)-N$ correlation observed here for elastocaloric materials could, in principle, apply to other caloric materials (i.e., magnetocaloric and electrocaloric materials). Even though the data on fatigue behavior of other caloric materials are somewhat limited (Table S1), our preliminary analysis indicates that the same correlation holds for them as well. Caloric materials based on first-order transitions with reported low cyclability (e.g., <10,000 cycles) can potentially have their functional fatigue lives extended if their $\Delta E/E$ can be decreased by, for instance, materials processing.

The conventional wisdom in the SMA community is that presence of non-equiatomic phases such as Ni_3Ti in the NiTi matrix is detrimental to materials integrity as the presence of brittle phases precipitated along grain boundaries can lead to fracture from local stress concentration (51) and mismatch stress generated by transformation-induced shape distortions in neighboring grains (52). The non-equiatomic phases have also plagued the self-propagating high-temperature synthesis used for porous Ni-Ti materials for decades as they occur inevitably and produce chemical inhomogeneity in porous implants (53). We created a Ni-Ti -based elastocaloric material whose exceptional stability and unusual operational efficiency are, in fact, derived from their unique and intricate nanocomposite structures made by additive manufacturing. This demonstration opens the door for the implementation of additive

manufacturing to caloric cooling in general providing much-desired topology flexibility in materials components that serve as both refrigerants and heat exchangers.

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5 the supplementary materials.

Supplementary Materials:

Materials and Methods

Supplementary Text

Figs. S1 to S8

5 Table S1

References (54–85)



Supplementary Materials for

Fatigue-resistant high-performance elastocaloric materials via additive manufacturing

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Materials and Methods

Materials fabrication

Additive manufacturing of Ni–Ti nanocomposite materials was carried out by using an L-DED system, Laser Engineered Net Shaping (LENSTM) (MR-7, Optomec Inc.) equipped with a 1 kW (1,064 nm wavelength) IPG Yb-fiber laser, four-nozzle coaxial powder feeders, and a motion control system. Two powder feeders were used to separately deliver elemental Ni and Ti powders (size $\approx 45\text{--}88\ \mu\text{m}$ for Ni (purchased from American Elements) and $\approx 45\text{--}106\ \mu\text{m}$ for Ti (purchased from AP&C Advanced Powders & Coatings Inc.); purity $>99.9\%$; gas-atomized) and the rotational speed of each feeder was used to control the mass flow rate of powders in order to tailor the mixing ratio and thus material composition. A laser beam with a spot size of 0.5–1.0 mm and a Gaussian intensity distribution created a molten pool on a Titanium plate substrate for flowing powders in a high-purity argon environment ($< 1.0\ \mu\text{L L}^{-1}$ oxygen). A three-dimensional computer-aided design model was used to guide the laser paths of contour and hatch for consecutive tracks on one layer and progressive movement along the Z-direction to generate subsequent layers. A continuous scan strategy was applied with a unidirectional scanning direction. The inverse of dimensionless hatch spacing, which is beam radius divided by hatch spacing, was optimized to be 2.0–3.0 and the dimensionless volumetric energy density (required to melt the powders in a single scan) was tuned to be 1.7–4.3 (supplementary text). The varied parameters yielded a sample density of $\approx 98.9\%$. Within a $300\ \text{mm}^3$ work envelope, cylindric parts were built with a dimensionless layer thickness ≈ 6.8 (Fig. S1) for laboratory tests, while tubular and honeycomb-shaped parts were built with a dimensionless layer thickness ≈ 0.7 as exemplified geometries. Possessing an enhanced surface-to-volume ratio is not only beneficial for heat exchange and thus allows high operating frequencies in elastocaloric cooling, but also reduces the cross-sectional area of the metallic refrigerants and thus can lower the required load (a product of stress and area) for transformation.

The material compositions were characterized using wavelength dispersive spectroscopy (Electron Probe Microanalyzer 8900R, JEOL Inc.) with calibrated standards, after sequential polishing with a final $0.05\ \mu\text{m}$ surface finish. Differential scanning calorimetry (Q100, TA Instruments) was performed at a scanning rate of $10\ \text{K min}^{-1}$ per ASTM F2004–05 standard. Post-fabrication heat treatments (54) were conducted in a high-temperature tube furnace (Lindberg/Blue M, Thermo Fisher Scientific Inc.) at a heating rate of $10\ \text{K min}^{-1}$ under argon environment (Fig. S6). Melt-casted tubes of $\text{Ni}_{50.8}\text{Ti}_{49.2}$ at.% alloys were purchased from Confluent Medical Technologies Inc., and melt-casted bars of $\text{Cu}_{68}\text{Zn}_{16}\text{Al}_{16}$ at.% alloys were synthesized at Ames Laboratory. The materials were machined into the dimensions of test specimens with a length-to-diameter ratio of ≈ 2 per ASTM E9 standard: L-DED produced Ni–Ti nanocomposite, 10.0 mm in length and 5.0 mm in diameter in a rod form; melt-casted $\text{Ni}_{50.8}\text{Ti}_{49.2}$, 4.7 mm in outer diameter, 3.8 mm in inner diameter, and 10.0 mm in length in a tube form; melt-casted $\text{Cu}_{68}\text{Zn}_{16}\text{Al}_{16}$, 8.0 mm in diameter and 17.9 mm in length in a rod form.

Mechanical and elastocaloric cooling testing

Uniaxial compressions were conducted on the machined specimens at room temperature using a servohydraulic load frame (810, MTS Systems Corp.) equipped with

a load cell of 250 kN. A factory-calibrated extensometer with a gauge length of 5.0 mm (632.29F-30, MTS Systems Corp.) was used to record the strains. The temperature of the specimens was measured using T-type thermocouples (nominal size of 0.5 mm \times 0.8 mm) attached to the middle of the specimens, recorded using a data recorder (cDAQ-9171, National Instruments Corp.), and stored using a LabVIEW program. Mechanical pre-treatment was conducted to initiate fully recoverable behaviors for L-DED produced Ni–Ti nanocomposite (Fig. S5), and ten mechanical cycles were performed on the melt-casted alloys to obtain stabilized hysteresis area. Compression experiments were independently performed more than twice on each material. The strain at which maximum transformation was achieved was 1.5%–1.9% for L-DED produced Ni–Ti nanocomposite, \approx 5.0% for melt-casted Cu₆₈Zn₁₆Al₁₆, and \approx 4.3% for melt-casted Ni_{50.8}Ti_{49.2}.

Mechanical cycling tests were performed in a displacement-controlled mode with a sinusoidal loading profile at room temperature. After conversion, the nominal mean strain, ϵ_m , was set to 2.0% with a strain amplitude, $\Delta\epsilon/2$, of 1.8% to keep the specimen subjected to compressive stress throughout the cycles. The cycle frequency was 0.05–0.1 Hz, which was about the same as that of operative cycles in cooling prototype systems (15, 55). 1,000,000 cycles were conducted for more than four months, and then the materials were tested to compare with the initial state.

Microstructure characterization

A focused ion beam microscope (Helios NanoLab G3 UC, Thermo Fisher Scientific Inc.) equipped with a micromanipulator was used to prepare transmission electron microscopy (TEM) specimens by lifting out lamellae along the build direction of the materials and thinning down to \sim 100 nm thickness under 30 kV, followed by a sequential cleaning under 5 kV and 2 kV. Scanning electron microscopy (SEM) images were collected at an accelerating voltage of 10 kV and a working distance of 4.0 mm. TEM observations were performed using a probe-corrected scanning transmission electron microscope (STEM) (Titan Themis 300, FEI Company) operated under an accelerating voltage of 200 kV. High-angle annular dark-field (HAADF) STEM images were acquired in a detection range of 99–200 mrad at a probe convergence angle of 18 mrad, and the dispersive X-ray spectroscopy (EDS) spectra and maps were collected using a Super-X EDS detector.

In situ compression testing during X-ray diffraction

In situ compression testing was performed during synchrotron X-ray diffraction measurements using the third generation Rotational and Axial Motion System (RAMS3) (56, 57) load frame at the Sector 1-ID-E hutch of the Advanced Photon Source (APS) at Argonne National Laboratory. A 1.2 mm wide by 1.0 mm tall monochromatic X-ray beam with 71.6 keV energy was used to illuminate the gage of the 1.0 \times 1.0 \times 2.0 mm³ parallelepiped compression specimen. During both loading and unloading, at load increments of 150 MPa between 0 and 1,500 MPa compressive loads, diffraction patterns were recorded every 0.5° of sample rotation on a GE-41RT area detector (58) located 1,449.3 mm away from the specimen as the specimen was rotated from 0° to 360° about the loading axis.

To analyze phase fraction evolutions with loads, all images collected for each load step were summed and integrated into a single histogram, and Rietveld refinement was then performed using GSAS-II (59). In performing the refinements, the structures of the majority Ni_3Ti and NiTiB_2 phases were firstly used in the refinement model, allowing lattice strains and microstrains to refine for both phases. Despite averaging the diffraction data over all sample rotations about the loading axis, the data still showed signatures of texture, especially for the Ni_3Ti phase. This texture was indicative of directional solidification and growth in L-DED processes (23). Then, sixth and tenth order spherical harmonics functions were used in modeling the NiTiB_2 and Ni_3Ti phases, respectively. After the majority phases were fit, the non-transforming, minority Ni and $\text{Ti}_4\text{Ni}_2\text{O}$ phases (Fig. S7) were then added to the model. While the lattice strain and microstrain parameters were stable for the $\text{Ti}_4\text{Ni}_2\text{O}$ phase, the microstrain for the Ni phase had to be manually adjusted and fixed. The same refinement strategy was then used for the first four loading steps (150, 300, 450, 600 MPa). The same phase fractions were determined for 0, 150, and 300 MPa loads within a fitting standard deviation. At 450 MPa, the refinement changed, indicating that NiTiB_2 was transforming to $\text{NiTiB}_{19'}$. To fit the martensite phase, the phase fractions of the non-transforming phases were fixed, and the NiTiB_2 and $\text{NiTiB}_{19'}$ phase fractions were refined against each other, in addition to lattice and microstrains for all phases, starting with the peak load (1,500 MPa), and working toward 450 MPa, for both loading and unloading data. The Rietveld model fit to the data for 0 and 1,500 MPa load, including the difference between the measured data and the Rietveld model, was visualized in Fig. S8.

Constitutive modeling

Abaqus finite element models of $1.0 \times 1.0 \text{ mm}^2$ size with sectional thicknesses of 0.1 mm were made to mimic the aspect ratios of NiTi versus Ni_3Ti morphologies experimentally observed in Fig. 11. The models were meshed using approximately 21,000 4-node doubly curved S4 elements with 0.01 mm size. Elements were assigned to belong to either a transforming NiTi phase or a non-transforming phase, with phase assignments mimicking the observed microstructures as reasonable as possible considering the mesh size. The non-transforming phase was assumed to be a volume-averaged mixture of Ni_3Ti , $\text{Ti}_4\text{Ni}_2\text{O}$, and Ni (volume fractions) according to the quantitative analysis of synchrotron X-ray diffraction patterns. More specifically, an equivalent non-transforming phase was defined with the effective Young's modulus, $\tilde{E} = 0.85 \times E_{\text{Ni}_3\text{Ti}} + 0.1 \times E_{\text{Ti}_4\text{Ni}_2\text{O}} + 0.05 \times E_{\text{Ni}}$, and Poisson's ratio, $\tilde{\nu} = 0.85 \times \nu_{\text{Ni}_3\text{Ti}} + 0.1 \times \nu_{\text{Ti}_4\text{Ni}_2\text{O}} + 0.05 \times \nu_{\text{Ni}}$, where Young's modulus and Poisson's ratio for Ni_3Ti , $\text{Ti}_4\text{Ni}_2\text{O}$, and Ni are 235 GPa, 44 GPa, and 200 GPa, and 0.28, 0.35, and 0.31, respectively. Models made using 40%, 50%, and 60% volume fractions of these non-transforming phases were used in the simulations. The transforming NiTi phase was simulated using the superelastic model that was built into Abaqus with $E_{\text{NiTi-B}_2} = 46 \text{ GPa}$, $E_{\text{NiTi-B}_{19'}} = 28 \text{ GPa}$, $\nu_{\text{NiTi-B}_2} = 0.33$, $\nu_{\text{NiTi-B}_{19'}} = 0.33$, σ_M^s (start stress for forward transformation into martensite) = 300 MPa, σ_M^f (finish stress for forward transformation into martensite) = 500 MPa, σ_A^s (start stress for reverse transformation into austenite) = 250 MPa, σ_A^f (finish stress for reverse transformation into austenite) = 50 MPa, and ε_L (transformation strain) = 5%. "Static" load type was used in Abaqus with 10^6 increments per load/unload step.

Thermodynamic analysis

Elastocaloric materials coefficient of performance $COP_{\text{materials}}$ were computed based on the thermodynamic analysis of our custom single-stage elastocaloric testing system (15), where the elastocaloric materials exhibit a uniform temperature profile at T_h (the temperature at hot heat exchanger) and T_c (the temperature at cold heat exchanger). The elastocaloric Brayton-like cycle consists of isentropic (adiabatic) loading and unloading processes, and two heat transfer processes under constant stress fields. The elastocaloric Stirling-like cycle consists of isothermal loading and unloading processes, and two heat transfer processes under constant stress fields. By merging thermodynamics-based equations (60) with hysteresis-contained Eq. 1, we make a universal form of $COP_{\text{materials}}$ in Eq. S1:

$$COP_{\text{materials}} = \frac{T_c \cdot \Delta s - \Delta E / 2}{(T_h - T_c) \cdot \Delta s + \Delta E} \quad (\text{eq. S1})$$

Here, Δs is computed using $\Delta s = q / T_c$, where q is the absorbed heat, which can be obtained using ΔT_{ad} as $q = C_p \times \Delta T_{\text{ad}}$ with a specific heat capacity C_p of $550 \text{ J kg}^{-1} \text{ K}^{-1}$ (Ni–Ti) and $420 \text{ J kg}^{-1} \text{ K}^{-1}$ (Cu–Zn–Al), or by $\Delta H_{\text{M} \rightarrow \text{A}}$ via $q = \Delta H_{\text{M} \rightarrow \text{A}}$. Materials densities ρ are $6,500 \text{ kg m}^{-3}$ for Ni–Ti and $7,700 \text{ kg m}^{-3}$ for Cu–Zn–Al. T_h and T_c are set to be 308 K and 300 K, respectively, to be consistent with AHRI Standard 210/240. Here, Carnot $COP = \frac{T_c}{(T_h - T_c)} = 37.5$.

Supplementary Text

Optimization of processing parameters in L-DED

To optimize processing parameters, we have selected a recommended processing window in a normalized processing diagram (26, 61). The dimensionless volumetric energy density, E^* , is defined in Eq. S2 (26, 62):

$$E^* = \frac{p^*}{v^* \cdot l^*} = \frac{A \cdot p}{2 \cdot v \cdot l \cdot r_b \cdot \rho \cdot C_p \cdot (T_m - T_0)} \quad (\text{eq. S2})$$

where $p^* = \frac{A \cdot p}{r_b \cdot k \cdot (T_m - T_0)}$ is the dimensionless laser power, $v^* = \frac{v \cdot r_b}{D}$ is the dimensionless laser scanning speed, $l^* = \frac{2 \cdot l}{r_b}$ is the dimensionless layer thickness, A is the surface absorptivity (≈ 0.26) (63), p is the laser power, v is the laser scanning speed, l is the layer thickness, r_b is the beam radius, ρ is the density, C_p is the specific heat capacity, T_m is the melting temperature, and T_0 is the initial temperature of the material. Besides, $h^* = \frac{h}{r_b}$ is the dimensionless hatch spacing. In the combinations of processing parameters, we keep $1/h^*$ to be 2.0–3.0 and E^* to be 1.7–4.3.

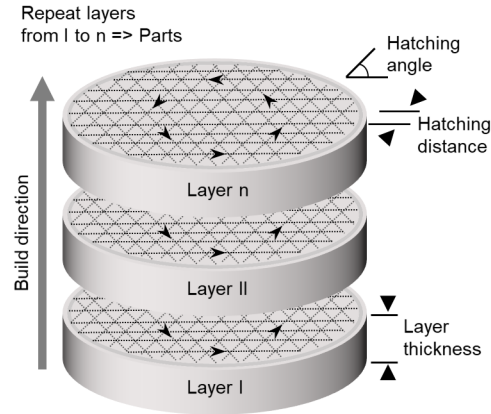


Fig. S1.

Design strategy of in situ thermal processing. Schematic representation of building an extended thickness in a layer and multiple hatching on the same layer for Ni–Ti nanocomposite rods. The dimensionless layer thickness is 6.8, and the inverse of dimensionless hatch spacing is 3.0. The laser beam passes six times on each layer as the hatching angle is changed by 60° with each run. This process results in imparting intense thermal energy, similar to the multiple melting-remelting processes in the conventional melt-casting method (64).

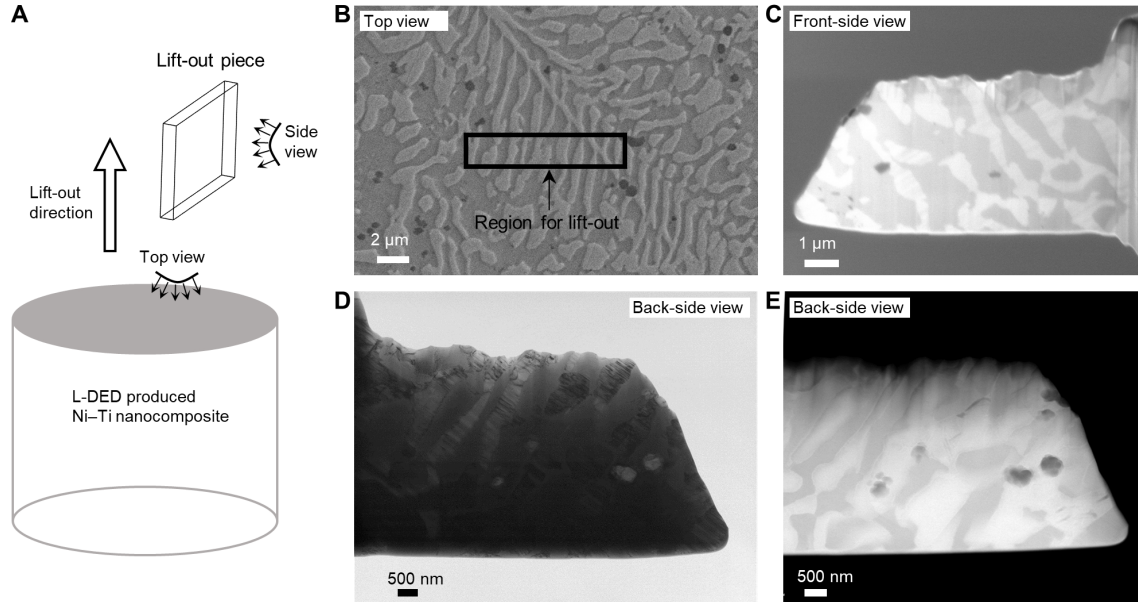


Fig. S2

Typical microstructure morphology. (A) Schematic showing the lift-out of a slice from the L-DED produced Ni-Ti nanocomposite. (B) SEM image of the specimen surface from a top view showing the region for lifting. (C) SEM image of the lateral cross-section surface from a front-side view showing a co-existence of the NiTi and Ni₃Ti phases. (D) TEM diffraction-contrast image from a back-side view showing the morphology and inner structure of the NiTi and Ni₃Ti phases. (E) STEM image from a back-side view showing the distinct compositions of the NiTi phase versus the Ni₃Ti phase.

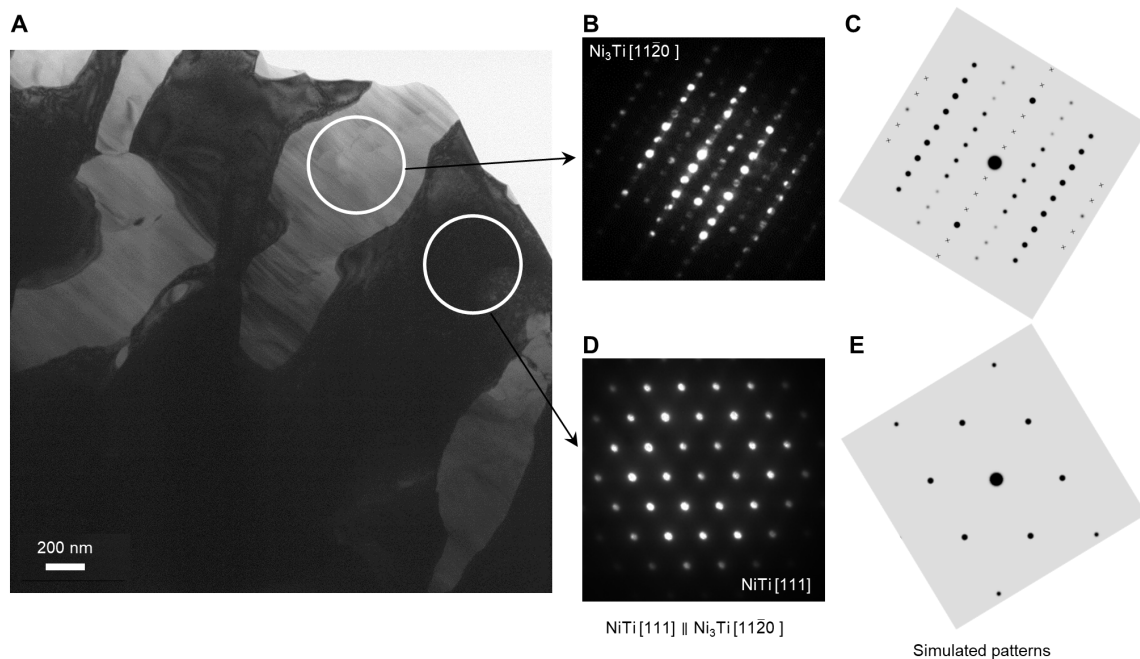


Fig. S3

Structures analyzed by electron diffractions. (A) TEM image showing the co-existence of the NiTi phase and the Ni_3Ti phase in the L-DED produced Ni-Ti nanocomposite. (B and C) Selected area diffraction patterns (B) and simulated patterns (C) confirming the Ni_3Ti phase at a zone axis of $[11\bar{2}0]$. (D and E) Selected area diffraction patterns (D) and simulated patterns (E) confirming the NiTi phase at a zone axis of $[111]$.

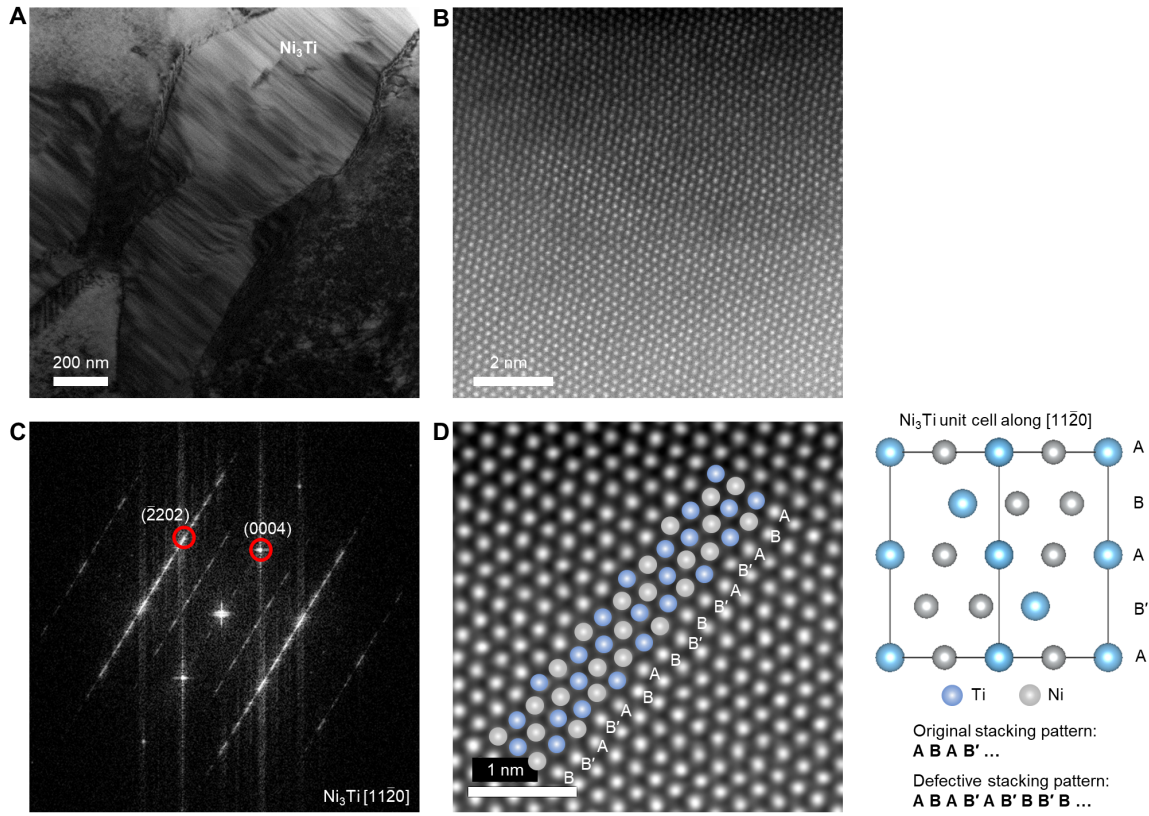


Fig. S4

Stacking faults in the Ni_3Ti phase. (A) TEM diffraction-contrast image showing stacking faults within Ni_3Ti in the L-DED produced Ni–Ti nanocomposite. (B) High-resolution HAADF image along Ni_3Ti [1120]. (C) FFT of (B). The streaks indicate the existence of the stacking faults. (D) Atomic-scale HAADF image with overlaid atomic models showing the defective stacking sequence. The regular stacking patterns of $\text{ABAB}'\dots$ has been changed into $\text{ABAB}'\text{AB}'\text{BB}'\text{B}\dots$ due to the stacking faults.

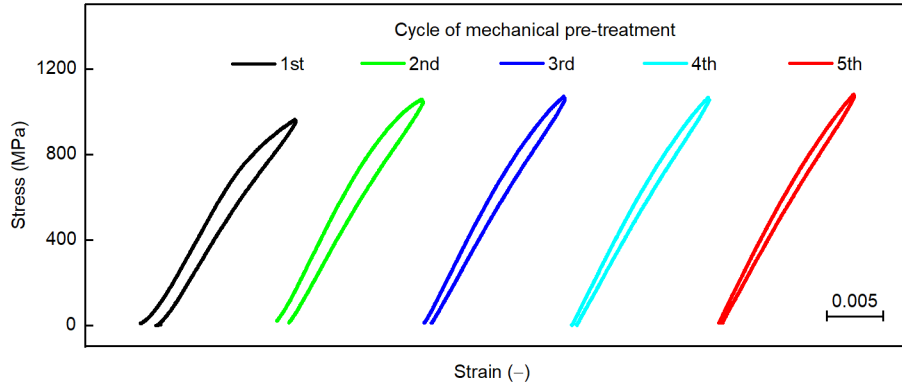


Fig. S5

Mechanical pre-treatment for fully recoverable behaviors. Mechanical pre-treatment is carried out on L-DED produced Ni-Ti nanocomposite to attain reversibility. Initial compressive treatment during the first four cycles leads to a small residual strain upon unloading, a signature of progressing plastic deformation to relax local stress, which could come from Ni_3Ti phase, and can also be facilitated by the defects such as stacking faults inside the Ni_3Ti phase (seen in Fig. S4). Starting with the fifth cycle, the increment in plastic deformation per cycle is negligible, indicating that the Ni-Ti nanocomposite has reached the shakedown state (65, 66); that is, beyond this point, further deformation of Ni_3Ti phase is elastic due to the properly self-organized pre-straining and pre-stressing.

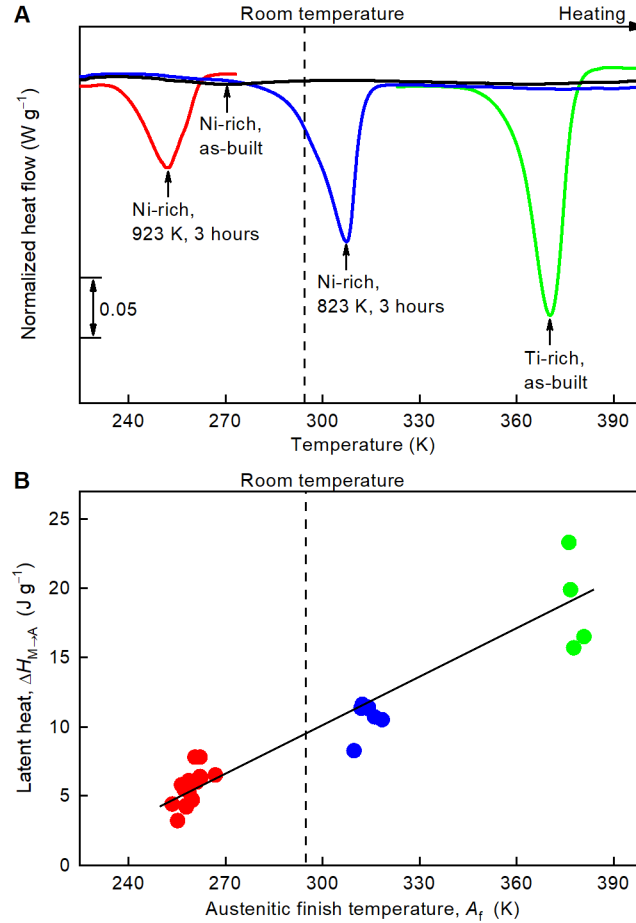


Fig. S6

Tuned martensitic transformation toward room temperature. (A) Differential scanning calorimetry thermo-grams of L-DED produced Ni-rich (51.5 at.% Ni) and Ti-rich (47.1 at.% Ni) materials after heat treatments, displaying the phase transformation trend near or below room temperature. (B) The plot of austenitic finish temperature, A_f , versus endothermic latent heat, $\Delta H_{M \rightarrow A}$, displaying the wide range of the transformation temperatures and the latent heat. In (B), the solid line is a guide to the eye.

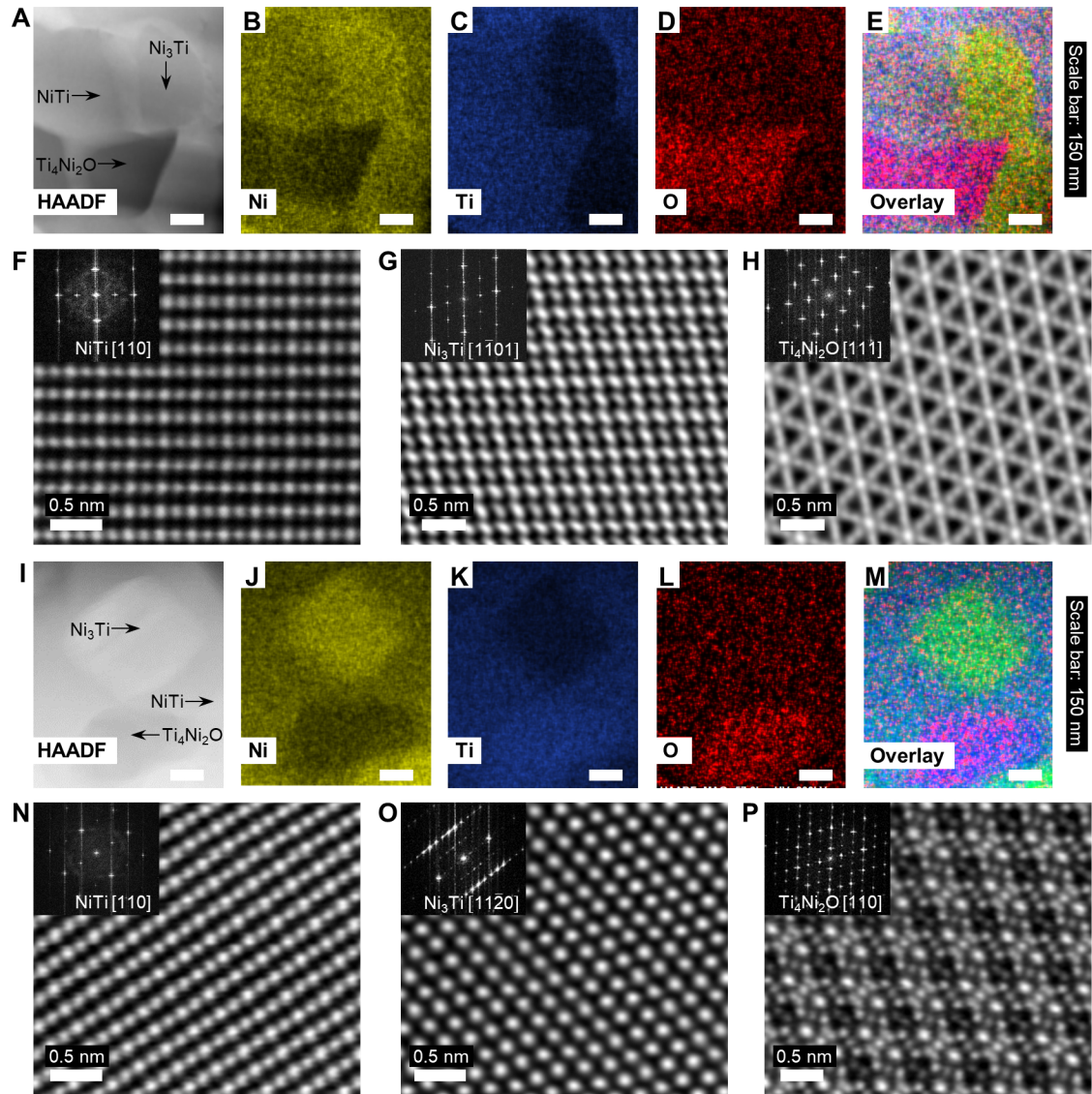


Fig. S7

Energy-dispersive X-ray spectroscopy (EDS) analysis and HAADF imaging. (A)–(P) L-DED produced Ni–Ti nanocomposite after heat treatment of (A)–(H) 923 K for 3 hours and (I)–(P) 823 K for 3 hours. (A)–(E) and (I)–(M) HAADF-STEM image (A), (I), EDS mapping of Ni (B), (J), Ti (C), (K), and O (D), (L), and overlay EDS maps (E), (M). (F)–(H) and (N)–(P) Atomic-scale HAADF images of NiTi (F), (N), Ni₃Ti (G), (O), and Ti₄Ni₂O phases (H), (P) with the corresponding fast Fourier transform (FFT) image and the zone axis at the top-left corner.

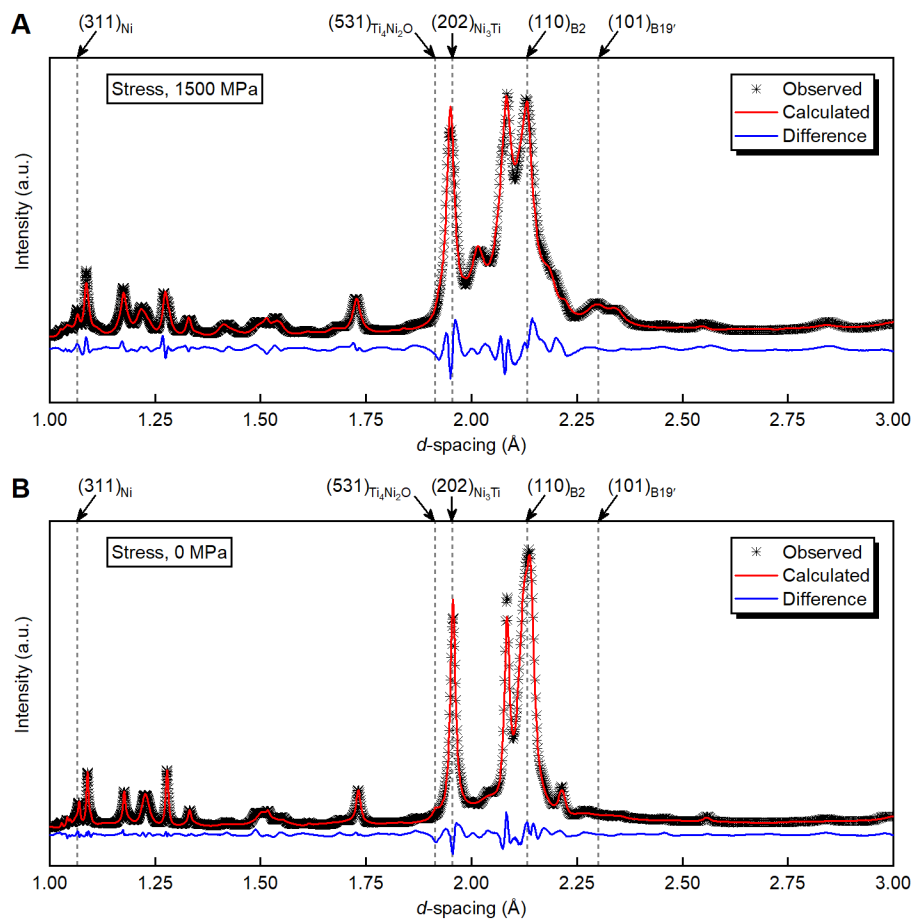


Fig. S8

Quantitative Rietveld refinement. (A and B) Rietveld refinement on high-resolution synchrotron X-ray diffraction patterns at a stress level of 1,500 MPa (A) and 0 MPa (B) to determine the present phases and their volume fractions. Ni_3Ti , $\text{Ti}_4\text{Ni}_2\text{O}$, and Ni have a volume fraction of $50.3 \pm 0.7\%$, $5.2 \pm 0.3\%$, and $0.8 \pm 0.1\%$, respectively. At a stress level of 0 MPa, NiTiB_2 has a volume fraction of $43.7 \pm 0.6\%$; at a stress level of 1,500 MPa, NiTiB_2 and $\text{NiTi}_{\text{B}_{19}'}$ have a volume fraction of $10.9 \pm 0.6\%$ and $33.7 \pm 0.6\%$, respectively. Roughly 50% of the nanocomposite being non-transforming precipitates is consistent with the measured latent heat of 5.6 ± 1.3 (mean \pm SD) J g^{-1} : they would correspond to 14.3 ± 3.3 J g^{-1} for the transforming fraction (NiTi) of the composite, well within the range of reported values (11, 13, 64).

Table S1.

Number of tested cycles for fatigue behavior of caloric materials reported in the literature.

Materials (at.%)	T (K)	$\Delta E/E$ (%)	$\Delta \varepsilon/2$ * (%)	N (–)	Reference	Caloric type & alloy category
Ni _{51.5} Ti _{48.5} (P)	294	6.9	1.8	>1,000,000	This work	Elastocaloric, Ni–Ti-based
Ni _{50.8} Ti _{49.2} (P)	294	33.8	1.8	>110,000	This work	
Ni _{50.8} Ti _{49.2} (S)	313	18.3	≈1.5	>10,000	(67)	
Ni _{50.9} Ti _{49.1} (P)	300	34.2	0.5	>100,000	(68)	
Ni ₅₀ Ti _{45.3} V _{4.7} (P)	298	27.5	≈1.9	>5,000	(69)	
Ti ₅₄ Ni ₃₄ Cu ₁₂ (P)	343	17.6	≈0.5	>10 ⁷ **	(42)	
Cu ₆₈ Zn ₁₆ Al ₁₆ (P)	293	44.9	2.0	>2,700	This work	Elastocaloric, Cu-based
Cu _{59.1} Zn ₂₇ Al _{13.8} (S)	343	15.6	≈2.5	>10,000	(67)	
Cu ₇₂ Al ₁₇ Mn ₁₁ (S)	293	30.9	2.0	>10,900	(70, 71)	
Ni ₅₄ Fe ₁₉ Ga ₂₇ (S)	323	18.3	≈2.0	>10,000	(67)	Elastocaloric, magnetic
Ni ₅₄ Fe ₁₉ Ga ₂₇ (P)	298	42.8	≈1.5	>100	(72)	
Ni ₅₀ Fe ₁₉ Ga ₂₇ Co ₄ (S)	348	12.3	≈2.5	>3,000	(73)	
Ni _{50.4} Mn _{27.3} Ga _{22.3} (P)	327	44.0	≈1.4	>100	(74)	
Ni _{48.4} Mn _{34.8} In _{16.8} (P)	313	68.0	≈0.5	>10	(75, 76)	
Ni _{51.3} Mn _{32.9} In _{15.5} B _{0.3} (P)	303	25.6	≈1.1	>150	(76)	
Ni ₄₅ Mn _{36.4} In _{13.6} Co ₅ (P)	296	51.9	≈1.5	>15	(77)	
Co ₅₀ Ni ₂₀ Ga ₃₀ (P)	299	30.9	≈2.0	>100	(78)	
Zn ₄₅ Au ₃₀ Cu ₂₅	298	8.0	≈2.2	>100,000	(43, 79)	Lattice- compatible
LaFe _{11.6} Si _{1.4} (P)	198	20.0	–	4	(80)	Magnetocaloric
LaFe _{11.6} Si _{1.4} (P; porous)	198	11.1	–	800	(80)	
MnFe _{0.95} P _{0.595} B _{0.075} Si _{0.33} (P)	278	2.8	–	>10,000 (ΔT_{ad} = 2.6 K)	(81, 82)	
BaTiO ₃ (S)	293	46.4	–	10	(83)	Electrocaloric
Ba(Zr _{0.2} Ti _{0.8})O ₃ (P)	300	11.5	–	100,000 (ΔT_{ad} = 0.2 K)	(84)	
Fe ₄₉ Rh ₅₁ (P)	–	–	–	50–100	(85)	Barocaloric***

T : Test temperature, $\Delta E/E$: dissipated fraction of input energy, $\Delta \varepsilon/2$: strain amplitude, and N : sustained cycles. “S” in parenthesis stands for single crystal, and “P” stands for polycrystal. “Lattice-compatible” refers to the alloy whose lattice parameters meet the mathematical relation that gives rise to a high degree of compatibility between phases (43). The $\Delta E/E$ can be evaluated for elastocaloric materials from stress–strain (σ – ε) plot, for magnetocaloric materials from magnetization–applied magnetic field (M – H) plot, and for electrocaloric materials from polarization–applied electric field (P – E) plot.

* An exact value is listed when the value is explicitly stated in the reference. Otherwise, an approximate value is extracted from the reference.

** The materials are in thin-film form with a thickness of 18 μm , and there are no cooling data reported in that reference.

*** In the reference, the cycle number is by indirect methods.